Fabrication of zinc coatings on alumina balls from zinc powder by mechanical coating technique and the process analysis

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Abstract

Mechanical coating technique was used to fabricate zinc (Zn) coatings on alumina (Al2O3) balls. The detailed evolution of the coatings was examined. The effect of the rotation speed of planetary ball mill on the evolution was investigated by experiments and modeling. The results showed that continuous and high dense Zn coatings with the average thickness of about 100 μm were formed during the milling operation at 300 rpm. To form continuous Zn coatings, a critical collision pressure corresponding to a critical minimum rotation speed was necessary to produce a critical plastic strain of Zn particles. Exponential relations between the required time to form continuous Zn coatings and the collision strength or the collision power were established. The relations showed that the required time was determined by the collision stress or the work done on Zn particles on unit area in unit time. The evolution of the coatings can fall into nucleation, formation and coalescence of discrete islands, formation and thickening of continuous coatings, and exfoliation of continuous coatings.

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1. Introduction

Ball milling, which is well known for mechanical alloying, is widely used to fabricate a variety of equilibrium and non-equilibrium materials that are difficult or impossible to be obtained by traditional techniques [1]. However, people have been assailed by the contamination during the process. The contamination mainly comes from the interfusion of grinding medium into milled powder or the adhesion of milled powder on grinding medium. Several attempts have been made in recent years to minimize the contamination during the process [1].


The procedure of mechanical coating technique is as follows. Firstly, Al2O3 balls are coated with metal powder by ball milling to form metal coatings on the surfaces of Al2O3 balls. Secondly, ball milling is used again to deposit TiO2 powder on the metal coatings that formed before. Eventually, TiO2/metal composite photocatalyst films are fabricated. There are two reasons for us to prepare metal coatings in the first step of mechanical coating. In our early works, it was found that the direct coating of TiO2 powder on Al2O3 balls by ball milling was very difficult and the coatings were easy to peel off. However, the coating of metal powder on Al2O3 balls was very easy and strong. In addition, the adhesive strength between TiO2 powder and metal coatings was large enough. The other reason is the improvement of charge separation efficiency. According to the effect of charge separation [8], the photogenerated electrons in TiO2 could be restrained. That can improve the photocatalytic activity of TiO2. The work functions of different metals are different. Therefore, we will make attempts to prepare different metal coatings and then fabricate TiO2/metal composite coatings to enhance the photocatalytic activity of TiO2. To apply the TiO2/metal composite photocatalyst films in the near future, Al2O3 balls with the diameter of 1 mm were used as the substrates for their low price. The small size of the substrates can increase the specific surface area of TiO2 and therefore increase the photocatalytic activity.

Although the welding and fracture of metal powders during ball milling have been studied by Maurice et al. [9–11], investigation on formation and evolution of metallic coatings during the process is scarce by now. Although Ti coatings [6] and Fe coatings [12] were
fabricated, it is still unsure that whether other metallic coatings can be formed on Al₂O₃ balls. The universal law for the formation and evolution of metallic coatings on Al₂O₃ balls during ball milling needs to be clarified. The detailed evolution of metallic coatings and its influencing factors are still unknown. In addition, the evolution of metallic coatings during the process is also important to the fabrication of TiO₂-metal composite photocatalyst films. From the above analysis, we studied a new kind of metal zinc rather than titanium or iron.

In this work ball milling was used to fabricate Zn coatings on Al₂O₃ balls. The coatings were characterized and the detailed evolution of the coatings during the process was discussed. The effect of the rotation speed of the planetary ball mill on the evolution was also investigated.

2. Experimental

2.1. Fabrication of Zn coatings

Zn powder (Niraco Co., Ltd.) and Al₂O₃ balls (Nikkato Co., Ltd.) were used as the coating material and the substrates respectively with the relevant parameters listed in Table 1. They were put into a bowl made of Al₂O₃ with a volume of 250 mL. The ball-to-powder weight ratio was 6:7. Mechanical coating was performed by a planetary ball mill (Pulverisette 6, Fritsch) with the parameters listed in Table 2. The rotation speed of the planetary ball mill was set at 300 rpm. The milling time was 4, 8, 12, 16, 20, 26, and 32 h. To decrease the influence of the air atmosphere, the sealed bowl was closed and no samples were taken before the desired samples were completed. To investigate the influence of the rotation speed on the evolution of Zn coatings, the rotation speeds were set at 100, 200, 250 and 400 rpm in the contrast tests. The milling time was 2, 3, 4, 8, 12, 16, 20, 26, 32 and 40 h. To ensure the safety during the process, a 10-minute milling operation was followed by a 2-minute cooling interval in order to avoid an excessive heating of the bowl although a temperature rise may promote the welding between metal powder particles. The schematic diagram can be found in our published work [12].

2.2. Characterization of Zn coatings

Before the characterization of the Zn-coated Al₂O₃ balls, they were treated by ultrasonic cleaning (frequency: 28 kHz) in acetone to remove the Zn particles that did not strongly adhere to the surfaces of Al₂O₃ balls. XRD analyzer (JDX-3530, JEOL) with Cu Kα radiation was used to determine the phase composition and the change of the surface coverage of Al₂O₃ balls with Zn. The surface morphology and the microstructure of the cross sections of the Zn-coated Al₂O₃ balls were observed by SEM (JSM-6510, JEOL). The oxygen content in the surface layer of the coatings was measured in SEM by EDS. 50 Zn-coated Al₂O₃ balls were selected randomly and weighed for three times. The average values were used to determine the weight evolution of Zn coatings.

3. Results and discussion

3.1. Fabrication and characterization of Zn coatings

Fig. 1 shows the XRD patterns of the Zn-coated Al₂O₃ balls after the milling operation at 300 rpm. It can be seen that the diffraction peaks of Zn appeared when the milling time was 4 h. It means that Zn powder particles adhered to the surfaces of Al₂O₃ balls. The peaks of Zn became higher while those of Al₂O₃ became lower with increase in milling time till 12 h. It indicates that the surface coverage of Al₂O₃ balls with Zn increased. When the milling time came to 8 and 12 h, the peaks of Al₂O₃ could hardly be seen. It infers that the surfaces of Al₂O₃ balls were almost coated with Zn. In other words, continuous Zn coatings might be formed. However, with further increase in milling time from 16 h to 26 h, the peaks of Al₂O₃ became higher while those of Zn became lower. It should result from the surface exposure of Al₂O₃ balls due to the breakage of Zn coatings.

SEM images of the surfaces of the Zn-coated Al₂O₃ balls after the milling operation at 300 rpm are shown in Fig. 2. The areas of dark color of Al₂O₃ balls correspond to the surfaces of Al₂O₃ balls and the gray areas correspond to Zn coatings. From these images, the evolution of Zn coatings during the milling process can be clearly seen. More Zn powder particles adhered to the surfaces of Al₂O₃ balls with increase in milling time. When it came to 8 h, continuous Zn coatings formed (Fig. 2(b)). However, with further increase of milling time after 16 h, parts of Zn coatings began to peel off and the surfaces of Al₂O₃ balls exposed again (Fig. 2(e) and (f)).

SEM images of the cross sections of the Zn-coated Al₂O₃ balls after the milling operation at 300 rpm are shown in Fig. 3. Firstly, Zn

<table>
<thead>
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<th>Table 1</th>
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<td>Source materials for one coating procedure.</td>
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<tr>
<td>Raw material</td>
</tr>
<tr>
<td>Zn powder</td>
</tr>
<tr>
<td>Al₂O₃ balls</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of the Zn-coated Al₂O₃ balls after the milling operation at 300 rpm for different time.
powder particles adhered to the surfaces of Al$_2$O$_3$ balls and formed discrete islands of Zn (Fig. 3(a)). Then the surfaces of Al$_2$O$_3$ balls and the discrete islands of Zn were coated with more Zn particles. That resulted in the formation of continuous Zn coatings when it came to 8 h (Fig. 3(b)). With further increase in milling time, more Zn powder particles adhered to the coatings which increased the thickness of the coatings. The average thickness of the coatings was about 100 $\mu$m when the milling time came to 12 h (Fig. 3(c)). When the milling time came to 16 and 20 h, it was found that parts of the coatings delaminated (Fig. 3(d) and (e)). When it came to 26 h, the complete exfoliation of the coatings was found (Fig. 3(f)). It should be pointed out that the complete exfoliation of the coatings did not occur simultaneously. In other words, when it came to 26 h, the complete exfoliation can be found on some Al$_2$O$_3$ balls while cannot be seen on the other Al$_2$O$_3$ balls. Despite some discrepancies, the evolution of Zn coatings from the surface images (Fig. 2) and the cross sections (Fig. 3) followed the same pattern. In addition the results are in agreement with that given by Fig. 1.

Fig. 2 shows the SEM images of the surfaces of the Zn-coated Al$_2$O$_3$ balls after the milling operation at 300 rpm for different time: (a) 4 h, (b) 8 h, (c) 12 h, (d) 16 h, (e) 20 h and (f) 26 h. 

Fig. 4 shows the SEM images of the Zn coatings fabricated in the milling at 300 rpm for 12 h. From Fig. 4(a), the dispersoids in dark color and the gray matrix were confirmed to be alumina and zinc respectively. The dispersoids should come from the bowl and Al$_2$O$_3$ balls and inlaid in Zn coatings under the repeating collision. From Fig. 4(b) and (d), a small quantity of pores and microcracks were found in the surface or on the cross section of the coatings. It indicates that the coatings were high dense but not fully dense. The coatings closely adhered to the Al$_2$O$_3$ ball and no pore or cracks were found on the interface between them (Fig. 4(c)). All the samples were treated by ultrasonic cleaning before the characterization. Therefore, the adhesion between them might be strong. The oxygen content in the surface layer of Zn coatings was also monitored by EDS with the result shown in Fig. 5. It can be seen that the oxygen content increased from 0.10 wt.% to 1.59 wt.% with increase of milling time. It means that the coatings were oxidized slightly during the milling process.

The adhesion of Zn powder particles to the surfaces of Al$_2$O$_3$ balls was also examined. Fig. 6 shows the SEM images of the surfaces of Zn-
coated Al₂O₃ balls after the milling operation at 300 rpm for different milling time. At the initial stage, lamellar Zn particles adhered to the surfaces of Al₂O₃ balls or on the discrete islands of Zn (Fig. 6(a)). Subsequently, continuous Zn coatings were formed by the coalescence of the discrete islands (Fig. 6(b)). With further increase in milling time, the surfaces of the coatings became smooth and the adhesion trace seems to be not obvious (Fig. 6(a)–(e)).

3.2. Effect of rotation speed on evolution of Zn coatings

Fig. 7 shows the evolution of Zn coatings during the milling at different rotation speeds for different milling time. It can be found that the evolution of Zn coatings at 200 and 400 rpm was similar with that at 300 rpm (Fig. 2). It was noted that continuous Zn coatings did not form until 32 h during the milling at 200 rpm (Fig. 7(a)–(c)). Continuous Zn coatings were formed when milling time was only 4 h during the milling at 400 rpm (Fig. 7(e)). The required time to form continuous Zn coatings was 8 h during the milling at 300 rpm (Fig. 2(b)). It can be safely concluded that higher rotation speed accelerated the formation and exfoliation of continuous Zn coatings from Fig. 2 and Fig. 7. Continuous Zn coatings or discrete islands of Zn did not form during the milling at 100 rpm even when milling time came to 60 h. It indicates that the continuous Zn coatings could not be formed during the milling at 100 rpm.

The weight gain of 50 Al₂O₃ balls during the milling operation was monitored. From these data, the average thickness of Zn coatings was determined with the results shown in Fig. 8. It can be found that the average thickness firstly increased and reached their peaks after which decreased again no matter the rotation speeds were 200, 300 or 400 rpm. Higher rotation speed accelerated the evolution of average thickness. The result is in good agreement with the above analysis on the evolution of the coatings. 300 rpm was confirmed to be the optimum rotation speed to fabricate Zn coatings. Here it was noted that the maximum average thickness at 300 rpm was about 84 μm which was less than the value measured from SEM image in Fig. 3. That is because the calculation of average thickness from weight gain was performed assuming that the coatings were fully dense. Therefore, the fact that the coatings were not fully dense was proved again.

During planetary ball milling, the direct impact between grinding balls and the inner wall of the bowl rather than that between grinding balls themselves is considered to be the most efficient collision since grinding balls moved in the same direction [13]. Zn powder particles were trapped between Al₂O₃ balls and the inner wall the bowl during the milling process. The deformation of Zn particles can be regarded as the forging between two parallel plates because the volume of the trapped Zn particles was much smaller than the colliding bodies. Therefore, lamellar Zn particles were found to adhere to the surfaces of Al₂O₃ balls or Zn coatings (Fig. 6). Although the sliding and even rolling of Zn powder particles on the inner wall of the bowl did happen during the process, they had weak effect on the formation of the coatings and therefore were neglected in the following discussion.

The relative impact velocity, \( v_0 \), of an Al₂O₃ ball impacting on the inner wall of the bowl can be given by [14]

\[
v_0 = K_0 \omega_p R_p
\]

where \( R_p \) is the plate radius of the planetary ball mill; \( K_0 \) is a constant dependent on the geometry of mill and is given 1.06 (deg⁻¹) for a point grinding ball in planetary ball milling [14]; \( \omega_p \) is the rotation
speed (deg·s\(^{-1}\)). Therefore, the relative impact velocities, \(v_b\) of Al\(_2\)O\(_3\) balls during the milling at different rotation speed can be given by Eq. (1).

The maximum collision pressure, \(P_{\text{max}}\) when an Al\(_2\)O\(_3\) ball impacts with the inner wall of the bowl can be estimated by [10]

\[
P_{\text{max}} = 0.3521v_b^{0.4} \left( \frac{\rho}{E_{\text{eff}}} \right)^{0.2} \left( \frac{\beta-1}{\beta} \right)^{0.6} E_{\text{eff}}
\]

where \(\rho\) is the density of Al\(_2\)O\(_3\) balls (kg·m\(^{-3}\)); \(E_{\text{eff}}\) is the effective modulus of Al\(_2\)O\(_3\) (Pa); \(R_{\text{bowl}}\) is the radius of the bowl (m); \(R_{\text{ball}}\) is the radius of Al\(_2\)O\(_3\) balls (m). Substituting Eq. (3) into Eq. (2), it follows that

\[
P_{\text{max}} = av_b^{0.4}.
\]

Where \(a\) is a constant depending on the geometry of the planetary ball mill, the dimension of the bowl, the physical properties of grinding ball. In this work, it was calculated to be \(2.73 \times 10^9\) (Pa·s\(^{0.4}\)·m\(^{-0.4}\)).

Fig. 6. Adhesion of Zn powder particles to the surfaces of Al\(_2\)O\(_3\) balls during the milling operation at 300 rpm for different time: (a) 4 h, (b) 8 h, (c) 12 h, (d) 16 h and (e) 20 h.

Fig. 7. SEM images of the surfaces of the Zn-coated Al\(_2\)O\(_3\) balls after the milling operation at 200 and 400 rpm for different milling time: (a) 200 rpm, 20 h; (b) 200 rpm, 26 h; (c) 200 rpm, 32 h; (d) 400 rpm, 3 h; (e) 400 rpm, 4 h and (f) 400 rpm, 8 h.
The collision frequency, $\psi$ for an Al$_2$O$_3$ ball with the inner wall of the bowl during the milling can be evaluated by [14,15]  

$$\psi = K \left( \omega_p - \omega_b \right)$$  

(5)

where $\omega_b$ is the rotation speed of the planetary ball mill ($r\cdot s^{-1}$); $\omega_p$ is the rotation speed of the bowl and equal to $\omega_p/Tr$. $K$ is a constant depending on the ball diameter and has been evaluated to be approximately $1.5 \left( r^{-1} \right)$ for balls with a diameter of 8–10 mm. Because there is no data for the balls with the diameter of 1 mm, the influence of the ball diameter is neglected here. The value for the balls with the diameter of 8–10 mm will be used here to evaluate the collision frequency for an Al$_2$O$_3$ ball.

Here two new physical concepts were defined. The product of the maximum collision pressure, $P_{\max}$ and the collision frequency, $\psi$ was defined as the collision strength with the dimension of $N\cdot m^{-2}\cdot s^{-1}$. Its physical meaning is the force exerted on Zn particles on unit area in unit time. The product of the relative impact velocity, $v_p$ and the maximum collision pressure, $P_{\max}$ was defined as the collision power with the dimension of $J\cdot m^{-2}\cdot s^{-1}$. Its physical meaning is the work done on Zn particles on unit area in unit time.

The results calculated from Eqs. (1)–(5) and the required time to form continuous coatings are listed in Table 3. The obtained data of $v_p$, $P_{\max}$ and $\psi$ are consistent with those by other researchers [10,16–18]. Therefore, Eqs. (1)–(5) should be proper to describe the milling process in the present work. Continuous Zn coatings were formed during the milling at 200 rpm while could not be formed when the rotation speed was 100 rpm. It suggests that there was a critical rotation speed to form continuous Zn coatings between 100 and 200 rpm in the present work. From the table, the maximum collision pressure, $P_{\max}$ and the collision frequency, $\psi$ increased with the increase of the rotation speed (actually the relative impact velocity, $v_p$). Greater collision pressure can result in greater deformation strain of Zn powder particles. According to the cold-welding theory, cold welding happens only when the deformation strain of metal particles is greater than a critical value [13]. During the milling at 100 rpm, the deformation strain should be smaller than the critical value. Therefore, continuous coatings did not form.

![Fig. 8. Average thickness of the coatings as a function of milling time at different rotation speed.](image)

![Fig. 9. Required time to form continuous Zn coatings as a function of collision strength or collision power.](image)

Table 3

<table>
<thead>
<tr>
<th>$v_b$ (rpm)</th>
<th>$v_p$ (m/s)$^{-1}$</th>
<th>$P_{\max}$ ($\times 10^9$ Pa)</th>
<th>$\psi$ (Hz)</th>
<th>Collision strength ($\times 10^9$ N m$^{-2}$s$^{-1}$)</th>
<th>Collision power ($\times 10^9$ J m$^{-2}$s$^{-1}$)</th>
<th>$t^*$ (h)</th>
</tr>
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<tr>
<td>100</td>
<td>1.35</td>
<td>3.31</td>
<td>7.06</td>
<td>23.37</td>
<td>5.13</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>3.11</td>
<td>4.37</td>
<td>14.09</td>
<td>61.57</td>
<td>13.59</td>
<td>32</td>
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<tr>
<td>250</td>
<td>3.88</td>
<td>4.77</td>
<td>17.63</td>
<td>84.10</td>
<td>18.51</td>
<td>16</td>
</tr>
<tr>
<td>300</td>
<td>4.66</td>
<td>5.13</td>
<td>21.15</td>
<td>108.50</td>
<td>23.91</td>
<td>8</td>
</tr>
<tr>
<td>400</td>
<td>6.22</td>
<td>5.76</td>
<td>28.21</td>
<td>162.49</td>
<td>35.83</td>
<td>4</td>
</tr>
</tbody>
</table>

$^*$ $t$ is the required time to form continuous coatings.
Conclusions

Continuous and high dense Zn coatings on Al₂O₃ balls were fabricated by mechanical coating technique. The formation of the coatings was a dynamic process of the adhesion of Zn clusters to the surfaces of Al₂O₃ balls and the cold welding between Zn particles. The evolution of the coatings can fall into nucleation, formation and coalescence of discrete islands, formation and thickening of continuous coatings, and exfoliation of continuous coatings. After peeling off the Zn coating at a certain stage, the internal stress weakened the adhesion of the coatings to the surfaces of Al₂O₃ balls. The evolution of the internal stress is similar with that during chemical vapor deposition (CVD) or physical vapor deposition (PVD) described by other researchers [20]. In addition, forging fracture could contribute to the exfoliation of the coatings. After repeating plastic deformation, Zn powder particles and continuous coatings became brittle due to the working hardening. When the Zn-coated Al₂O₃ balls collided with the inner wall of the bowl, a crack might initiate when a critical tensile strain was attained. Subsequently, crack propagation occurred when the plastic energy release rate exceeded a value characteristic of the material. Maurice and Courtney [9] have developed the fragmentation mechanisms of metal powder particles. In a word, the exfoliation of the continuous coatings resulted from the combined action of the internal stress and the external collision stress. The stage is called exfoliation of continuous coatings.

Here, it should be pointed out that all the stages might happen simultaneously but only one of them was dominant at a given interval. For example, the exfoliation of the coatings was observed when the formation and coalescence of discrete islands was dominant. Similarly, the formation and coalescence of discrete islands was also found when the exfoliation was dominant. In addition, higher rotation speed accelerated the evolution of the coatings and shortened the interval of each stage as discussed in Section 3.2. Interestingly, the evolution of Fe films during mechanical coating was very similar and also fell into the above four stages in our published work [12]. It suggests that the evolution of metal coatings may follow the same regularity.

The publication of Zn coatings on grinding balls indicates that mechanical coating is a promising technique to modify surface conditions and can improve a series of surface properties of materials.

References


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Hao is studying in Chiba University as a doctor candidate, the main investigation fields are the fabrication of metal coatings by mechanical coating technique, the preparation of TiO₂/metal composite photocatalyst films and the improvement of their photocatalytic activity.

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